Review of Thermodynamics

The equations of stellar structure involve derivatives of thermodynamic variables such as pressure, temperature, and density. To express these derivatives in a useful form, we will need to review the basic thermodynamic relations. First, let’s define the variables:

- $\rho$: the gas density
- $q$: the specific heat content
- $P$: the gas pressure
- $u$: the specific internal energy
- $T$: the gas temperature
- $s$: the specific entropy
- $\mu$: the mean molecular weight
- $V$: the specific volume ($1/\rho$)

Note that $q$, $u$, $s$, and $V$ are all per unit mass. From these variables come the specific heats

$$c_V = \left(\frac{dq}{dT}\right)_V = T \left(\frac{\partial s}{\partial T}\right)_V$$ (1.1)

$$c_P = \left(\frac{dq}{dT}\right)_P = T \left(\frac{\partial s}{\partial T}\right)_P$$ (1.2)

the ratio of the specific heats

$$\gamma = \frac{c_P}{c_V}$$ (1.3)

the adiabatic temperature gradient

$$\nabla_{ad} = \left(\frac{\partial \ln T}{\partial \ln P}\right)_s$$ (1.4)

an isothermal compressibility coefficient

$$\alpha = -\frac{P}{V} \left(\frac{\partial V}{\partial P}\right)_{T,\mu} = \left(\frac{\partial \ln \rho}{\partial \ln P}\right)_{T,\mu}$$ (1.5)
a volume coefficient of expansion

\[ \delta = \frac{T}{V} \left( \frac{\partial V}{\partial T} \right)_{P,\mu} = - \left( \frac{\partial \ln \rho}{\partial \ln T} \right)_{P,\mu} \] (1.6)

and a chemical potential coefficient

\[ \varphi = -\frac{\mu}{V} \left( \frac{\partial V}{\partial \mu} \right)_{P,T} = \left( \frac{\partial \ln \rho}{\partial \ln \mu} \right)_{P,T} \] (1.7)

(For the following, we will assume the chemical composition is fixed.)

We will also need the first law of thermodynamics:

\[ dq = Tds = du + P dV \] (1.8)

Note that although there are four variables in this equation (\(s, T, P,\) and \(V\)), only two are independent.
To derive the relationships between the various thermodynamic variables, first take $s$ and $V$ as independent, and re-write (1.8) as

$$du = Tds - PdV$$  \hspace{1cm} (1.9)

However, when written in terms of $s$ and $V$, $du$ is formally

$$du = \left( \frac{\partial u}{\partial s} \right)_V ds + \left( \frac{\partial u}{\partial V} \right)_s dV$$

which means that

$$\left( \frac{\partial u}{\partial s} \right)_V = T \quad \text{and} \quad \left( \frac{\partial u}{\partial V} \right)_s = -P$$  \hspace{1cm} (1.10)

Now, mathematically

$$\frac{\partial^2 u}{\partial V \partial s} = \frac{\partial^2 u}{\partial s \partial V}$$

so

$$\left( \frac{\partial}{\partial V} \right)_s \left( \frac{\partial u}{\partial s} \right)_V = \left( \frac{\partial}{\partial s} \right)_V \left( \frac{\partial u}{\partial V} \right)_s$$

or

$$\left( \frac{\partial T}{\partial V} \right)_s = -\left( \frac{\partial P}{\partial s} \right)_V$$  \hspace{1cm} (1.11)

Similarly, if we choose $s$ and $P$ as the independent variables, and add $d(PV)$ to each side of (1.9), then the first law of thermodynamics becomes

$$dH = d(u + PV) = Tds - PdV + PdV + VdP = Tds + VdP$$
The total first derivative of $H$ is then

$$dH = \left( \frac{\partial H}{\partial s} \right)_P ds + \left( \frac{\partial H}{\partial P} \right)_s dP$$

which implies that

$$\left( \frac{\partial H}{\partial s} \right)_P = T \quad \text{and} \quad \left( \frac{\partial H}{\partial P} \right)_s = V$$

and

$$\left( \frac{\partial T}{\partial P} \right)_s = \left( \frac{\partial V}{\partial s} \right)_P \quad (1.12)$$

If we subtract $d(Ts)$ from each side of the first law of thermodynamics, then $T$ and $V$ are the free parameters, via

$$dF = d(u - Ts) = Tds - PdV - Tds - sdT = -PdV - sdT$$

We then get the relations

$$\left( \frac{\partial F}{\partial T} \right)_V = -s \quad \text{and} \quad \left( \frac{\partial F}{\partial V} \right)_T = -P$$

which leads via the second derivatives to

$$\left( \frac{\partial s}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad (1.13)$$

Finally, if $T$ and $P$ are chosen to be independent, and $d(PV - Ts)$ are added to (1.8), then we can derive the relation

$$\left( \frac{\partial s}{\partial P} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_P \quad (1.14)$$
Thus, we have Maxwell’s relations

\[
(\frac{\partial T}{\partial V})_s = - (\frac{\partial P}{\partial s})_V \tag{1.11}
\]

\[
(\frac{\partial T}{\partial P})_s = (\frac{\partial V}{\partial s})_P \tag{1.12}
\]

\[
(\frac{\partial s}{\partial V})_T = (\frac{\partial P}{\partial T})_V \tag{1.13}
\]

\[
(\frac{\partial s}{\partial P})_T = - (\frac{\partial V}{\partial T})_P \tag{1.14}
\]
To derive a relation between the specific heats, start by letting $T$ and $P$ be independent, and write the specific heat content as

$$dq = T \, ds = T \left[ \left( \frac{\partial s}{\partial T} \right)_P \, dT + \left( \frac{\partial s}{\partial P} \right)_T \, dP \right]$$

and $dP$ as

$$dP = \left( \frac{\partial P}{\partial T} \right)_V \, dT + \left( \frac{\partial P}{\partial V} \right)_T \, dV$$

This gives

$$dq = T \left( \frac{\partial s}{\partial T} \right)_P \, dT + T \left( \frac{\partial s}{\partial P} \right)_T \left[ \left( \frac{\partial P}{\partial T} \right)_V \, dT + \left( \frac{\partial P}{\partial V} \right)_T \, dV \right]$$

We can now evaluate $(dq/dT)$ while holding $V$ constant, i.e., with $dV = 0$

$$\left( \frac{dq}{dT} \right)_V = T \left( \frac{\partial s}{\partial T} \right)_P + T \left( \frac{\partial s}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V$$

The term on the left side of the equation is $c_V$, the first term on the right is $c_P$, and $(ds/dP)_T = -(dV/dT)_P$ by a Maxwell relation (1.14). Thus,

$$c_P - c_V = T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial T} \right)_V$$

The first partial differential can immediately be written in terms of the volume coefficient of expansion (1.6)

$$\left( \frac{\partial V}{\partial T} \right)_P = \frac{V \delta}{T} \quad (1.15)$$
The second partial differential can also be re-written, if one first notes that the total derivative for $dV$ is

$$
\frac{dV}{dT} = \frac{\partial V}{\partial T} \text{ }_P \text{ } dT + \frac{\partial V}{\partial P} \text{ }_T \text{ } dP
$$

Thus, when $V$ is held constant, $dV = 0$, and

$$
\frac{\partial P}{\partial T} \text{ }_V = -\frac{\partial V}{\partial T} \text{ }_P \div \frac{\partial V}{\partial P} \text{ }_T
$$

The numerator on the right side is again $(\delta/\rho T)$, while the denominator is related to the compressibility coefficient by

$$
\frac{\partial V}{\partial P} \text{ }_T = -\frac{\alpha V}{P}
$$

Thus

$$
\frac{\partial P}{\partial T} \text{ }_V = \frac{P \delta}{T \alpha} \tag{1.16}
$$

and

$$
c_P - c_V = \frac{PV \delta^2}{T \alpha} = \frac{P \delta^2}{\rho T \alpha} \tag{1.17}
$$

Note that this reduces to $\mathcal{R} = k/m_A$ for an ideal gas.
Finally, to express the change in the heat content of a system, $dq$, in terms of the intensive parameters only, choose $V$ and $T$ as the independent variables, and write the change in entropy as

$$ds = \left( \frac{\partial s}{\partial T} \right)_V dT + \left( \frac{\partial s}{\partial V} \right)_T dV$$

Using the definition of heat capacity (1.1) and the Maxwell relation (1.13), this becomes

$$ds = \frac{c_V}{T}dT + \left( \frac{\partial P}{\partial T} \right)_V dV$$

If we now substitute (1.16) for $(\partial P/\partial T)_V$, and convert $dV$ to $d\rho$ using $dV = -1/\rho^2 d\rho$, we get an expression for $dq$

$$dq = T ds = c_V dT - \frac{P\delta d\rho}{\rho\alpha}$$

This can then be further simplified by noting that

$$\frac{d\rho}{\rho} = \left( \frac{\partial \ln \rho}{\partial \ln P} \right)_T d\ln P + \left( \frac{\partial \ln \rho}{\partial \ln T} \right)_P d\ln T = \alpha \frac{dP}{P} - \delta \frac{dT}{T}$$

Thus

$$dq = c_V dT + \frac{P\delta^2}{\rho T\alpha} dT - \frac{\delta}{\rho} dP$$

or

$$dq = c_P dT - \frac{\delta}{\rho} dP \quad (1.18)$$

This equation also leads directly to an expression for the adiabatic temperature gradient. If $dq = 0$, then

$$c_P dT = \frac{\delta}{\rho} dP$$
which implies that
\[
\left( \frac{\partial T}{\partial P} \right)_s = \frac{\delta}{\rho c_P}
\]
and
\[
\nabla_{ad} = \left( \frac{\partial \ln T}{\partial \ln P} \right)_s = \frac{P \delta}{T \rho c_P}
\]
(1.19)

Note that for an ideal gas, the definition of an adiabat implies that
\[
P \propto \rho^\gamma \propto \left( \frac{P}{T} \right)^\gamma \Rightarrow T \propto P^{(\gamma - 1)/\gamma}
\]

Hence for a monotonic gas with \( \gamma = 5/3 \),
\[
\nabla_{ad} = (2/3) \left/ (5/3) \right. = 0.4
\]
(1.20)

Note also that (1.19) can then be substituted back into (1.18) to yield an equation for \( dq \) in terms of \( P, T, c_P \), and adiabatic temperature gradient
\[
dq = c_PdT - \frac{Tc_P \nabla_{ad}}{P}dP = c_P T \left[ \frac{dT}{T} - \nabla_{ad} \frac{dP}{P} \right]
\]
(1.21)